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For: POLY(TRIMETHYLENE TEREPHTHALATE) AND PROCESS FOR PRODUCING THE SAME

VERIFIED TRANSLATION CERTIFICATE

Honorable Commissioner of Patents and Trademarks
Washington, D.C.   20231

Sir:

The undersigned, of the below address, hereby verifies that I well know both the English and __Japanese__ languages, and that the attached is a full, true literal and faithful translation into the English language of the __39__ page __Japanese__ language application which I am now advised carries U.S. Serial No. 10/066,712 effectively deposited in the United States Patent and Trademark Office on __February 6, 2002__.

The undersigned declares further that all statements made herein on personal knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 25th day of September 2002

DESCRIPTION

POLY(TRIMETHYLENE TEREPHTHALATE) AND PROCESS FOR PRODUCING THE SAME

Technical Field

The present invention relates to a poly(trimethylene terephthalate) and a process for producing the same. The present invention relates in more detail to a poly(trimethylene terephthalate) excellent in shade, oxidation resistance stability and melt stability, and a process for producing a poly(trimethylene terephthalate) having a molecular weight in a range from low to high even by polymerization on an industrial scale of the order of tons.

Background Art

A poly(trimethylene terephthalate) (hereinafter abbreviated to PTT) fiber obtained by melt spinning a polycondensation product of a lower alcohol ester of terephthalic acid or terephthalic acid and 1,3-propanediol (also termed trimethylene glycol, 1,3-propanediol being abbreviated to PDO below) has various excellent properties that cannot be obtained from a poly(ethylene terephthalate) (hereinafter abbreviated to PET) fiber, a nylon 6 fiber, and the like fiber, such as an astonishing soft feeling and drapability that have never been observed before, excellent stretchability, low temperature dye-affinity and weathering resistance. Asahi Chemical Corporation. has solved many technological problems associated with the polymerization, spinning, processing, development of commercial articles, and the like of a PTT, and has recently put a PTT fiber on the market for the first time in the world under the trade name of Solo.

As explained above, the technologies related to the production of fibers from PTT have been developed to the

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level of industrialization. However, the following
problems related to the polymerization of PTT still
remain unsolved: a poly(trimethylene terephthalate)
having a high intrinsic viscosity is difficult to obtain
5   by melt polymerization alone when polymerization is
carried out on an industrial scale, and the polymer tends
to be easily colored. The polymerization of PTT on an
industrial scale herein refers to polymerization on the
following scales: for batch polymerization,
10   polymerization on a scale of 0.3 t/batch or more,
preferably 1 t/batch or more; for continuous
polymerization, polymerization on a scale of 10 t/day or
more, preferably 50 t/day or more.

For example, polymerization of PTT becomes
15   understandable when the polycondensation reactivity of
PTT is compared with that of poly(butylene terephthalate)
(hereinafter abbreviated to PBT). For PBT, when
polymerization is conducted using a batch-wise
polymerizer equipped with a plate-like agitating blade in
20   the presence of a titanium alkoxide catalyst at 260°C as
will be explained in Comparative Example 1, the
polymerization degree increases with time. The
polymerization degree further increases even when the
polymer comes to have an intrinsic viscosity (intrinsic
25   viscosity of 1.4 dl/g or more, polymerization degree of
about 160) at which raking becomes difficult. In
contrast to PBT, when PTT is polymerized even under the
same polymerization conditions, the polymerization degree
reaches a peak near an intrinsic viscosity of 0.8 dl/g
30   (polymerization degree of about 100). Further extension
of the polymerization time lowers the polymerization
degree on the contrary. Moreover, such a peaking
phenomenon of the intrinsic viscosity (polymerization
degree) in the polymerization of PTT becomes more
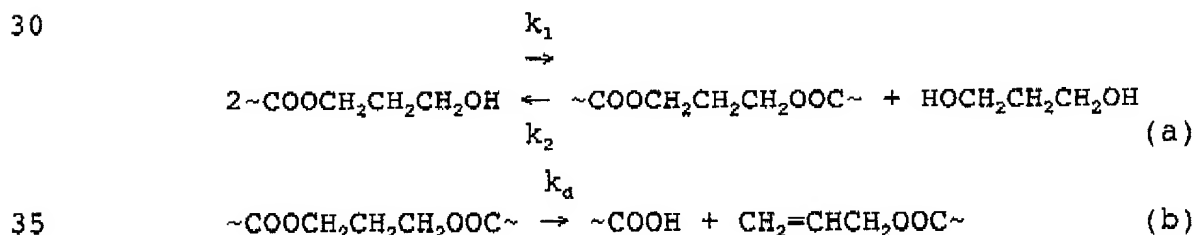35   significant when the polymerization scale becomes larger.

In order to use PTT for clothes and industrial
fibers, PTT usually must have an intrinsic viscosity of

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0.85 dl/g or more in view of the manifestation of the strength. However, production of PTT having such a viscosity by conventional melt polymerization alone on an industrial scale has been impossible. For example, USP
5   5,798,433 and EP 1,046,662 describe a process for producing PTT showing excellent whiteness and an intrinsic viscosity of 0.85 dl/g or more. However, the descriptions of both of these references are based on experiments carried out on a scale of no more than
10   several liters. Expansion of the polymerization scale in the disclosed process to an industrial scale only results in the production of a polymer having problems with quality such as mentioned below. The intrinsic viscosity of the polymer cannot be as high as 0.85 dl/g or more. A
15   polymer obtained by excessively extending the polymerization time is colored, or tends to be colored when used in the air for a long time. The polymer shows a decrease in the molecular weight in a large proportion during melt molding.
20   In order to establish a technology of polymerizing PTT having an intrinsic viscosity of 0.85 dl/g or more by melt polymerization alone even on an industrial scale, the present inventors have analyzed the cause of the peaking phenomenon of an intrinsic viscosity
25   (polymerization degree) in the melt polymerization of PTT, and clarified the following matter.
          Elementary reactions forming the polycondensation reaction of PTT are mainly the following two reactions:

30
$$2{\sim}COOCH_2CH_2CH_2OH \underset{k_2}{\overset{k_1}{\rightleftarrows}} {\sim}COOCH_2CH_2CH_2OOC{\sim} + HOCH_2CH_2CH_2OH \quad (a)$$

$$35 \quad {\sim}COOCH_2CH_2CH_2OOC{\sim} \overset{k_d}{\rightarrow} {\sim}COOH + CH_2{=}CHCH_2OOC{\sim} \quad (b)$$

The forward reaction is a chain growth reaction (formula

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(a)) effected by removal of PDO of two terminal hydroxyl groups. The backward reactions include a reaction in which the ester portion suffers decomposition with PDO that has not been excluded from the reaction system
5 (backward reaction of the formula (a)), and the thermal decomposition reaction (formula (b)) of the ester portion.

First, a case in which efficient discharge of PDO from the reaction system is achieved is considered. In
10 this case, because the equilibrium is inclined to the forward reaction side, the backward reaction of the formula (a) can be ignored. When the forward reaction alone of the formula (a) is dominant, the intrinsic viscosity monotonously increases with time. For example,
15 the polycondensation reactions of PET and PBT approximately correspond to the above reaction. However, for PTT, because the allyl terminal ($CH_2=CHCH_2OOC\sim$) of the thermal decomposition product is thermodynamically stabilized, the thermal decomposition reaction rate (k_d)
20 is significantly large. As a result, the reaction of the formula (b) contributes much in a relatively short period of time as the polycondensation reaction proceeds. The reaction of the formula (b) therefore becomes dominant over the forward reaction of the formula (a). The
25 levelling off phenomenon of the intrinsic viscosity in the melt polymerization of PTT as explained above is estimated to take place due to the dominant reaction of the formula (b).

Next, the case in which efficient discharge of PDO
30 is not achieved will be considered. For example, the case in which the scale of polymerization is extremely increased, that is, polymerization on an industrial scale corresponds thereto. When the polymerization scale is increased, the specific surface area of the reactant
35 drastically decreases. Discharge of PDO therefore becomes difficult, and PDO remaining in the reaction system breaks the ester bond of PTT (backward reaction of

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the formula (a)). As a result, contribution of the backward reaction of the formula (a) becomes significant, resulting in no increase in the intrinsic viscosity. The significant contribution is estimated be the reason why the peaking phenomenon of an intrinsic viscosity takes place in an early stage when the polymerization scale is increased.

Accordingly, the present inventors have discovered that the following procedures are essential as means for increasing a finally attained polymerization degree of PTT in melt polymerization alone regardless of the polymerization scale: inhibition of the backward reaction of the formula (a) and the reaction of the formula (b), namely, 1) advancement of the polycondensation reaction in a state in which the thermal decomposition reaction less contributes and 2) efficient discharge of PDO from the reaction system.

An object of the present invention is to provide a PTT excellent in shade, oxidation resistance stability and melt stability and having a molecular weight in a range from low to high even when the PTT is prepared by polymerization on an industrial scale. Another object of the present is to provide a polymerization process capable of producing a PTT having a molecular weight in a range from low to high regardless of the charging scale of the monomer in the polymerization of the PTT having excellent properties as mentioned above, more specifically to provide a polymerization process of PTT capable of inhibiting thermal decomposition in the polycondensation reaction and efficiently discharging PDO.

Brief Description of the Drawings

Fig. 1 schematically shows a polymerization apparatus used in the reaction example in Comparative Example 1 or 2, and an example of an agitating state of a reactant in the step of a polycondensation reaction.

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Fig. 2 schematically shows a polymerization apparatus used in the reactions in Examples 1, 3 and 8, and an example of an agitating state of a reactant in the step of a polycondensation reaction.

5   Fig. 3 schematically shows a polymerization apparatus used in the reactions in Examples 2 to 3, and an example of an agitating state of a reactant in the step of a polycondensation reaction.

Fig. 4 is a process flow chart showing an
10   arrangement example of a polymerizer in the embodiments of the present invention in a continuous polymerization process (Examples 4, 5).

In the figures, the reference numerals designate as follows:

15   100 --- rotary axis

101 --- solution surface of a reactant during stirring

102 --- reaction vessel

103 --- agitating blade

20   103a --- lower agitating blade

103b --- helical blade

104 --- temperature detector end

105 --- film-like reactant drips

106 --- fixed lattice

25   107 --- cylindrical reaction vessel

108 --- flow of a reactant

109 --- discharge direction of a polymer

110 --- motor

111 --- esterification reaction vessel

30   112 --- helical agitating blade

113 --- first polycondensation reaction vessel

114 --- second polycondensation reaction vessel

115 --- third polycondensation reaction vessel

116 --- disc type agitating blades

35   In addition, agitating blades in Fig. 4 are disc-like, and are each fixed to either one shaft or another shaft while the shaft are connected to two motors,

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respectively. The shafts are rotated therewith. The lower portion of any one of the blades fixed to the upper shaft except the left end one in the figure occupies a space between the upper portions of two adjacent lower blades fixed to the lower shaft. Rotation of the rotary shaft scrape up a reactant in the lower portion of the reaction vessel.

Disclosure of the Invention

In order to obtain a high molecular weight PTT by melt polymerization alone, the present inventors have investigated a polymerization process comprising inhibiting the thermal decomposition reaction and discharging PDO efficiently. As a result, they have found the possibility that a high molecular weight PTT can be produced when the polycondensation reaction is advanced while contribution of the thermal decomposition reaction is insignificant, that is, when discharge of PDO from the reaction system is conducted sufficiently (inhibition of the backward reaction in the formula (a)), and when the polycondensation reaction can be carried out in a short period of time (inhibition of the formula (b)) while there are many terminal hydroxyl groups. They therefore investigated in more detail and achieved the present invention.

That is, the first of the present inventions is a PTT comprising 80% by weight or more of trimethylene terephthalate units based on the entire repeating units, and satisfying the following conditions (1) and (2):

(1) the intrinsic viscosity is from 0.4 to 1.5 dl/g; and

(2) $[-OH]/([-OH] + [-COOH] + [-CH_2CH=CH_2]) \times 100 \geq 40$

The second of the present inventions is a process for producing a PTT wherein terephthalic acid or/and its lower alcohol ester is reacted with PDO to form PDO ester

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of terephthalic acid and/or its oligomer, and the
polycondensation reaction of the reactant is conducted to
give a PTT containing 80% by weight or more of
trimethylene terephthalate units based on the entire
5   repeating units, the process comprising conducting the
polycondensation reaction while the formula (1) is being
satisfied:

$$[-OH]/([-OH] + [-COOH] + [-CH_2CH=CH_2]) \times 100 \geqq 40 \qquad (1)$$

10 wherein $[-OH]$, $[-COOH]$ and $[-CH_2CH=CH_2]$ represent a
terminal hydroxyl group content, a terminal carboxyl
group content and a terminal allyl group content of the
poly(trimethylene terephthalate), respectively.

15   The PTT of the present invention is a PTT comprising
80% by weight or more of trimethylene terephthalate units
based on the entire repeating units.
        The PTT of the present invention may contain less
than 20% by weight of repeating units other than the
20 trimethylene terephthalate units based on the entire
repeating units. There is no specific limitation on the
monomer forming such repeating units as long as the
monomer is other than terephthalic acid or its lower
alcohol ester, and PDO; examples of the monomer include
25 diols, dicarboxylic acids, dicarboxylic acid esters,
dicarboxylic acid amides and oxycarboxylic acids.
Specific examples of the ester-forming monomer include
diols such as ethylene glycol, 1,2-propanediol, 1,4-
butanediol, 1,5-pentanediol, 1,6-hexanediol and 1,4-
30 cyclohexanedimethanol, dicarboxylic acids such as oxalic
acid, malonic acid, succinic acid, glutaric acid, adipic
acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid,
biphenyldicarboxylic acid, 5-sodium sulfoisophthalic
acid, 5-potassium sulfoisophthalic acid, 5-lithium
35 sulfoisophthalic acid, 2-sodium sulfoterephthalic acid,
2-potassium sulfoterephthalic acid, 4-sodium sulfo-2,6-
naphthalenedicarboxylic acid, 2-sodium sulfo-4-

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hydroxybenzoic acid and tetrabutylphosphonium 5-
sulfoisophthate, esters of such dicarboxylic acids with
lower alcohols such as methanol, oxycarboxylic acids such
as oxyacetic acid and oxybenzoic acid, esters of such
5   oxycarboxylic acids with lower alcohols such as methanol,
and polyols such as poly(ethylene glycol) and
poly(tetramethylene glycol) having a molecular weight of
from 200 to 100,000. Two or more types of ester-forming
monomers may optionally be copolymerized. Moreover, a
10   copolymerization component formed in the step of
polymerization, for example, a dimer of PDO (bis(3-
hydroxypropyl) ether, hereinafter abbreviated to BPE) may
be copolymerized. BPE is formed when PDO and 3-
hydroxypropyl group at the PTT molecular terminal further
15   react with PDO in the polymerization step, and further
copolymerized with a PTT without further processing.
Although BPE lowers the light resistance and heat
resistance of a PTT, suitable copolymerization of BPE has
the effects of increasing an exhaustion ratio of dye and
20   spinning stability. Suitable copolymerization of BPE is
therefore preferred, and BPE is copolymerized in a ratio
of from 0.01 to 2% by weight, preferably from 0.04 to
1.2% by weight based on the polymer weight. Moreover,
the PTT of the invention may contain a cyclic dimer
25   formed by dimerizing a trimethylene terephthalate unit in
an amount of 3% by weight or less based on the polymer
weight. When the amount exceeds 3% by weight, the PTT
unpreferably precipitates during molding to lower the
process stability. The polymer preferably contains the
30   cyclic dimer in an amount of 1.5% by weight or less, more
preferably 1.2% by weight or less, still more preferably
0.7% by weight or less in view of no presence of a
spinning step and dyeing step, decreased yarn breakage
and uneven dyeing.
35   The PTT of the present invention must have an
intrinsic viscosity of from 0.4 to 1.5 dl/g. A PTT
having an intrinsic viscosity of less than 0.4 dl/g

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becomes brittle, and is hard to handle. Moreover, a yarn
obtained therefrom shows a low strength. There is no
specific limitation on the upper limit of an intrinsic
viscosity. However, when the intrinsic viscosity exceeds
5   1.5 dl/g, the PTT shows an excessively high melt
viscosity. As a result, metering the PTT with a gear
pump cannot be conducted smoothly, and the spinnability
is lowered due to faulty discharging. The intrinsic
viscosity of the PTT is preferably from 0.85 to 1.5 dl/g,
10   particularly preferably from 0.87 to 1.35 dl/g in view of
the manifestation of the strength of the yarn, resin,
film, and the like.

The PTT according to the present invention may be
copolymerized or mixed with various additives, for
15   example, delustering agents such as titanium oxide, heat
stabilizing agents, defoaming agents, orthochromatic
agents, flame retardants, antioxidants, ultraviolet-ray
absorbers, infrared-ray absorbers, nucleating agents,
fluorescent brighteners, and the like. In particular,
20   when titanium oxide is to be added as a delustering
agent, titanium oxide is added in an amount of from 0.01
to 3% by weight based on the weight of the polymer.

In the production process of the present invention,
use of heat stabilizing agents and coloring inhibitors is
25   particularly preferred as a method of increasing shade,
oxidation resistance stability and melt stability.
Pentavalent or trivalent phosphorus compounds and
hindered phenol antioxidants are preferred as heat
stabilizing agents. Examples of the pentavalent or
30   trivalent phosphorus compound include trimethyl
phosphate, triethyl phosphate, tributyl phosphate,
triphenyl phosphate, trimethyl phosphite, triethyl
phosphite, triphenyl phosphite, phosphoric acid and
phosphorus acid. Examples of the hindered phenol
35   antioxidants include pentaerythritol tetrakis[3-(3,5-di-
tert-butyl-4-hydroxyphenyl) propionate], 1,1,3-tris(2-
methyl-4-hydroxy -5-tert-butylphenyl)butane, 1,3,5-

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trimethyl-2,4-6-tris(3,5- di-tert-butyl-4-
hydroxybenzyl)benzene, 3,9-bis{2-[3-(3-tert -butyl-4-
hydroxy -5-methylphenyl)propionyloxy]-1,1-
dimethylethyl}-2,4,8,10-tetraoxaspiro[5,5]undecane,

5   1,3,5-tris(4-tert-butyl-3- hydroxy-2,6-
dimethylbenzene)isophthalic acid, triethylglycol bis[3-
(3-tert-butyl-5-methyl-4-hydroxyphenyl)propionate], 1,6-
hexanediol bis[3-(3,5-di-tert-butyl-4 -
hydroxyphenyl)propionate, 2,2-thio-diethylene-bis[3-(3,5-

10   di-tert-butyl-4-hydroxyphenyl)propionate] and octadecyl-
3- (3,5-di-tert-butyl-4-hydroxyphenyl)propionate]. These
substances may be added in an amount of from 0.01 to 0.5%
by weight, preferably from 0.02 to 0.1% by weight based
on the PTT in view of both the polymerization rate and

15   improvement of the whiteness. The addition amount is
from 2 to 250 ppm, preferably from 5 to 150 ppm,
particularly preferably from 10 to 150 ppm as an amount
of phosphorus element in the polymer. Examples of the
coloring inhibitor include cobalt compounds such as

20   cobalt acetate and cobalt formate, and commercially
available fluorescent brighteners. Such an inhibitor can
be added in an amount of from 0.0001 to 0.1% by weight
based on the PTT. These additives can be added at an
arbitrary stage of the polymerization.

25   The PTT of the present invention must have the value
of $[-OH]/([-OH] + [-COOH] + [-CH_2CH=CH_2]) \times 100$ being 40
or more, wherein $[-OH]$, $[-COOH]$ and $[-CH_2CH=CH_2]$
represent a terminal hydroxyl group content, a terminal
carboxyl group content and a terminal allyl group content

30   of the PTT, respectively. Although there is no specific
limitation on the units of these contents as long as the
same units are used, milli-equivalent/kg is usually used.
When the relationship is satisfied, a PTT excellent in
shade and melt stability is obtained. The value of $[-OH]/([-OH] + [-COOH] + [-CH_2CH=CH_2]) \times 100$ is preferably

35   OH]/([-OH] + [-COOH] + [-CH_2CH=CH_2]) \times 100$ is preferably
50 or more, more preferably 60 or more.

          Of the three types of terminal groups in the above

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formula, the specific values of [-COOH] and [-CH₂CH=CH₂]
are each preferably 35 mequivalent/kg polymer or less,
more preferably 25 mequivalent/kg polymer or less, most
preferably 20 mequivalent/kg polymer or less in view of

5   the melt stability and oxidation resistance stability of
the PTT.

    The PTT of the present invention preferably has an
L* value of 80 or more that shows a brightness of the
polymer, more preferably 85 or more, for the purpose of

10   realizing chromaticness of color during dyeing and the
use of a pigment. For the same reason, the PTT
preferably has a b* value of from -1 to 5 that represents
a yellowness of the polymer, more preferably from -0.5 to
4.

15   The PTT of the present invention can be produced by
a process wherein terephthalic acid or/and its lower
alcohol ester is reacted with PDO to form PDO ester of
terephthalic acid and/or its oligomer, and
polycondensation reaction of the reactant is conducted to

20   give a PTT containing 80% by weight or more of
trimethylene terephthalate units based on the entire
repeating units, the process comprising conducting the
polycondensation reaction while the formula (1) is being
satisfied:

25

$[-OH]/([-OH] + [-COOH] + [-CH_2CH=CH_2]) \times 100 \geqq 40$ (1)

wherein [-OH], [-COOH] and [-CH₂CH=CH₂] represent a
terminal hydroxyl group content, a terminal carboxyl
group content and a terminal allyl group content of the

30   PTT, respectively.

    In the present invention, a known method can be used
as the method of forming PDO ester of terephthalic acid
and/or its oligomer by reacting terephthalic acid or/and

35   its lower alcohol ester.

    The reaction is called an esterification reaction
when terephthalic acid is used, and an ester interchange

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reaction when a lower alcohol ester of terephthalic acid is used. Examples of the lower alcohol ester of terephthalic acid include dimethyl terephthalate, diethyl terephthalate and monomethyl terephthalate.

5   Terephthalic acid, a lower alcohol ester of terephthalic acid and PDO may be commercially available compounds, or they may also be recovered from PTT and PTT products. Their purity is preferably 95% or more, more preferably 98% or more, most preferably 99% or more. A

10   lower alcohol ester of terephthalic acid is preferred to terephthalic acid in view of the polymerization rate, whiteness, oxidation resistance stability and melt stability of the PTT thus obtained, and it is also preferred in view of the ease with which the

15   copolymerization ratio of BPE can be lowered. Of impurities contained in PDO, carbonyl group-containing compounds are preferred to be contained in an amount by weight of 1,000 ppm or less, more preferably 500 ppm or less based on the weight of the polymer in view of the

20   whiteness of the polymer.

The charging ratio of PDO to terephthalic acid or a lower alcohol ester of terephthalic acid that is a polymerization starting material is preferably from 0.8 to 3 in terms of a molar ratio. When the charging ratio

25   is less than 0.8, the ester interchange reaction hardly proceeds, and the finally attained intrinsic viscosity is small when the polycondensation reaction is finished. Moreover, when the charging ratio is greater than 3, the melting point is lowered, and the whiteness of the

30   polymer tends to be lowered. The charging ratio is preferably from 1.4 to 2.5, more preferably from 1.5 to 2.3.

In order to allow the reaction to proceed smoothly, a catalyst is preferably used. Examples of the catalyst

35   include titanium alkoxides represented by titanium tetrabutoxide and titanium tetraisopropoxide, metal oxides such as amorphous titanium oxide precipitates,

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amorphous titanium oxide/silica coprecipitates and amorphous zirconia precipitates, and metal carboxylates such as calcium acetate, manganese acetate, cobalt acetate and antimony acetate. Use of such a substance in

5   an amount of from 0.01 to 0.2% by weight, preferably from 0.05 to 0.12% by weight based on the entire carboxylic acid component monomers is preferred in view of the reaction rate, whiteness of the polymer and thermal stability. The reaction temperature is 150°C or more,

10   preferably from about 200 to 250°C. The reaction can be conducted while by-product water and an alcohol such as methanol are being distilled off. The reaction time is usually from 2 to 10 hours, preferably from 2 to 4 hours. The reactant thus obtained is a PDO ester of terephthalic

15   acid or/and its oligomer. The esterification reaction and ester interchange reaction may optionally be conducted successively and continuously in two or more reaction vessels.

A PTT can be produced by subjecting the PDO ester of

20   terephthalic acid or/and its oligomer to a polycondensation reaction.

In the polycondensation reaction, a titanium alkoxide represented by titanium tetrabutoxide and titanium tetraisopropoxide or a metal oxide such as

25   amorphous titanium oxide precipitate, amorphous titanium oxide/silica coprecipitates and amorphous zirconia precipitate is optionally added in an amount of from 0.01 to 0.2% by weight, preferably from 0.03 to 0.15% by weight based on the entire carboxylic acid component

30   monomers. When the amount of the catalyst is extremely large, a thermal decomposition takes place, and the formula (1) to be described later is not satisfied. Moreover, when the amount is too small, the polymerization degree cannot be increased. The catalyst

35   used in the esterification reaction and ester interchange reaction can be used as the polycondensation catalyst without further processing. Alternatively, the catalyst

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may be newly added. Of these catalysts, titanium-based
catalysts are effective for any of the esterification
reaction, ester interchange reaction and polycondensation
reaction. The titanium-based catalysts are therefore the
5   most preferred ones for the following reasons. When a
titanium-based catalyst is added at the stage of the
ester interchange reaction or polycondensation reaction,
the polycondensation reaction can be conducted without
newly adding it prior to the polycondensation reaction or
10 by adding only a small amount even when the addition is
necessary.
       The polycondensation reaction must be conducted
while the formula (1) is being satisfied:

15 $[-OH]/([-OH] + [-COOH] + [-CH_2CH=CH_2]) \times 100 \geq 40$ (1)
wherein $[-OH]$, $[-COOH]$ and $[-CH_2CH=CH_2]$ represent the
hydroxyl content, carboxyl content and allyl group
content at the molecular terminals of the PTT,
respectively. In addition, the unit in the [] is
20 mequivalent/kg polymer.

       The molecular terminals of the PTT are principally a
hydroxyl group, a carboxyl group and an allyl group.
       The left term of the inequality in the formula (1)
25 shows the proportion of hydroxyl groups to the entire
molecular terminal groups in the PTT that is being formed
or that is to be formed. In the present invention, the
left term must be 40% or more. When the value is less
than 40%, contribution of the thermal decomposition
30 reaction and discharge of PDO is slowed, and the
intrinsic viscosity cannot attain 0.85 dl/g. Because the
carboxyl groups and allyl groups are also a measure of
the degree of thermal decomposition, the magnitude of the
left term is preferably 50% or more, more preferably 55%
35 or more, in view of not only the rate of attaining a
desired polymerization degree but also the shade,
oxidation resistance stability and melt stability of the

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polymer thus obtained.

A specific method of conducting the polycondensation reaction while the formula (1) is being satisfied is required to conduct discharge of PDO at high efficiency
5   and to complete the polycondensation reaction before a drastic thermal decomposition of the PTT takes place. Such a polymerization method is recommended to satisfy the following two conditions: 1) the polycondensation reaction is conducted at temperature as low as possible
10   so that a thermal decomposition hardly takes place; and 2) a polycondensation reactant is continuously raked upside from the deepest portion of the reaction vessel to form a thin film so that the discharge efficiency of PDO is enhanced, and the film is continually renewed so that
15   PDO is discharged from the new surface. That is to say, the catalyst, stirring, vacuum degree, an amount of the catalyst, and the like in the polycondensation reaction must be adjusted so that the formula (1) is satisfied.

The temperature suited to 1) is preferably from 235
20   to 270°C, particularly preferably from 245 to 265°C. In addition, when the reaction temperature is raised while a large amount of PDO remains, the copolymerization ratio of BPE tends to exceed 2% by weight. It is therefore preferred that the reaction temperature be not raised to
25   255°C or more until the remaining amount of PDO becomes 5% or less. Moreover, it is particularly preferred to conduct polycondensation reaction while the formula (2) mentioned below is being satisfied when the intrinsic viscosity of the polycondensation reactant is 0.5 dl/g or
30   more, as a polymerization procedure satisfying 2). The vacuum degree during the polycondensation reaction is from 0.0001 to 2 torr, preferably from 0.01 to 0.7 torr.

$$S/V \geqq 0.07 \qquad \text{formula (2)}$$

35   S: total surface area (cm^2) of the polycondensation reactant

V: weight (g) of the polycondensation reactant

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S herein designates a total surface area of the
portion of the polycondensation reactant contacted with
the gas phase (that may be in a reduced pressure state)
when the polycondensation reaction is conducted.

A specific method of measuring S will be shown
below. The total surface area of the polycondensation
product that is contacted with the gas phase is the sum
of the following three terms: (a) the solution surface of
the reactant present in the lower portion of the reaction
vessel; (b) the surface of the reactant adhering to the
agitating blade; and (c) the surface of the film-like
reactant dripping from the agitating blade. S is
measured by procedures as explained below. The interior
of the polymerizer during stirring is visually observed,
or pictures thereof are taken with a camera, or a film
thereof is made with a video camera, or the like, and the
surface state of the reactant is observed.

For example, when a reaction vessel as shown in Fig.
1 is used, it can be concluded from the observation of
the polycondensation reaction taking place in the
reaction vessel that (a) alone should be determined
because neither (b) nor (b) is present. The cross-
sectional area S of a reaction vessel 102 substantially
corresponds to S.

When a helical blade as shown in Fig. 2 is used and
rotated in the direction to rake the reactant upside, the
following phenomenon is observed. The reactant solution
surface forms a reverse cone as shown in Fig. 2; the
raked reactant adheres to the blade, is raised up, and
finally drips on the reactant solution in the lower
portion. Accordingly, the surface area in (a) can be
determined by assuming the solution surface photographed
with a camera to be a cone. The area in (b) can be
determined from the front and back surfaces of a portion
of the blade from the solution surface to the part where

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adhesion of the reactant disappears. The area in (c) can
be determined by taking a picture of a dripping reactant
at an instant, and obtaining the area of both surfaces
from the picture. Because (c) varies to some extent with
5   time, it is preferred to take the picture five times, and
to obtain the average value of the five pictures. S can
be obtained by totaling (a), (b) and (c) thus obtained.
In addition, when a helical blade as shown in Fig. 2 is
used, rotation of the rotary axis in the direction at
10   which the reactant is raked downside forms a reactant
surface as shown in Fig. 1. The rotary direction of the
rotary axis therefore becomes important.

    When the reactant is allowed to creep over a fixed
lattice and fall down as shown in Fig. 3, neither (a) nor
15   (b) is present. The solution surface covered by the
reactant at the stage of the polycondensation reaction is
therefore photographed, and the area of the front and
back surfaces (corresponding to (c)) is defined as S.

    A horizontal agitation reaction apparatus as shown
20   in Fig. 4 is similar to the apparatus in Fig. 2. In this
case, the surface area is as follows: (a) is an area of
the solution surface present in the lower portion of the
reaction vessel; (b) is the sum of the front and back
surface areas of the portion of agitating blades above
25   the solution surface; and (c) is obtained in the same
manner as in Fig. 2 by taking pictures with a camera.

    The specific method of calculating S as explained
above produces an error to some extent depending on the
movement of the reactant. However, there is little
30   arbitrariness by the operator making measurements, and
the accuracy is sufficient for the definition of the
present invention. On the other hand, V is a theoretical
weight of a polymer obtained from the starting material
placed in the vessel. Because the polycondensation
35   reactant to be reacted has a fairly high polymerization
degree, the weight is about equal to the theoretical
weight of the polymer. For the polycondensation reaction

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in Fig. 4, the theoretical weight is equal to the weight of the polymer present in the reaction vessel in a stationary state.

The S/V ratio designates a surface area per unit
5   weight of the polycondensation reactant, and represents the degree of surface renewal of the reactant during the polycondensation reaction. A larger value of S/V signifies that the surface renewal is actively conducted. As a result, removal of PDO that is a by-product is
10   promoted, and the extent to which the reaction is influenced by the thermal decomposition is decreased. The polymerization degree can therefore be increased in a short period of time.

When the S/V ratio is less than 0.07 cm^2/g,
15   efficient removal of PDO becomes difficult, and production of a PTT having a high polymerization degree, that is an object of the present invention, becomes difficult. Although a larger S/V ratio is better, an S/V ratio of 100 cm^2/g or less is preferred in view of the
20   size of the polymerization vessel. An S/V ratio is preferably 0.1 cm^2/g or more, more preferably 0.15 cm^2/g or more. Moreover, the surface of the polycondensation reactant to be reacted is preferably continually renewed.

In addition, the condition for satisfying the
25   formula (2) is that the reactant has an intrinsic viscosity of 0.5 dl/g or more. When the intrinsic viscosity is less than 0.5 dl/g, the reactant shows a low melt viscosity. As a result, satisfaction of the formula (2) is meaningless because discharge of PDO is easy even
30   when the S/V ratio is less than 0.07 cm^2/g. Satisfaction of the formula (2) does not become an optimum condition for efficient discharge of PDO until the reactant has an intrinsic viscosity of 0.5 dl/g or more at which diffusion of PDO in the reactant and discharge of PDO
35   from the surface thereof becomes difficult. The formula (2) may be easily satisfied even when the reactant has an intrinsic viscosity of less than 0.5 dl/g.

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When the formula (2) is satisfied, it is preferred that the reactant be made to continually form a film by stirring. A preferred polymerization process forms, during the polymerization step, a film having a thickness

5 of 20 mm or less, preferably 10 mm or less, most preferably 1 mm or less. Preferred polycondensation vessels where such a polycondensation reaction as mentioned above is conducted include: a vessel wherein PDO ester of terephthalic acid or/and its oligomer

10 obtained by an esterification reaction or ester interchange reaction is allowed to fall along a thin rod or lattice to form a film; a vessel wherein the ester or/and its oligomer in a film-like state are allowed to slide down along a slope; and a vessel wherein the ester

15 or/and its oligomer are continuously raked up from the polymerization vessel with a helical blade, a cage-like blade, or the like, and they are made filmy during raking or during dripping after raking.

 The process for producing a PTT of the present

20 invention can be applied to both batch polymerization and continuous polymerization. It is important that the continuous polymerization includes at least the steps to be explained below in view of the polymerization reactivity, and the shade, oxidation resistance stability

25 and melt stability of the polymer thus obtained. That is, it is preferred to use the following reaction vessel and polymerization apparatus: a reaction vessel for conducting at least one ester interchange reaction or/and esterification reaction to which terephthalic acid or/and

30 its lower alcohol ester and PDO are continuously fed, and in which PDO ester of terephthalic acid and/or its oligomer can be continuously formed; and a polymerization apparatus in which two or more polycondensation reaction vessels are successively connected. Although one

35 polycondensation reaction vessel may be used, at least two or more, preferably three or more polycondensation reaction vessels should be connected in series and used.

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The polycondensation reactant increases its
polymerization degree as the product passes a plurality
of the polycondensation reaction vessels. It is
preferred to increase the reaction temperature and vacuum
5   degree as the number of reaction vessels the reactant
passes increases. The reactant preferably has an
intrinsic viscosity of 0.3 dl/g or more, preferably 0.5
dl/g or more until it reaches the final polycondensation
vessel.

10   The PTT thus obtained can be pelletized by a known
method, and used as a raw material for fibers, molded
articles and films. Moreover, the PTT may be fed to a
molding machine to form fibers or films, or it may be
injection molded or extrusion molded. Examples of the
15   fiber include filaments, short fibers, side-by-side
yarns, monofilament yarns and unwoven fabrics.

Moreover, in order to increase the polymerization
degree of the PTT and decrease an amount of the cyclic
oligomer, the PTT thus obtained may be subjected to solid
20   phase polymerization. The PTT of the invention compared
with the other PTTs shows a high solid phase
polymerization rate, and is excellent in shade, oxidation
resistance stability and melt stability. A known method
can be applied as the solid phase polymerization method.
25   That is, the PTT of the invention in pellets, powder, a
fibrous state, a plate-like state, a block-like state, or
the like state can be polymerized in a solid phase at
temperature of from 170 to 220°C for 3 to 100 hours in
the presence of inert gas such as nitrogen or argon, or
30   under a reduced pressure of 100 torr or lower, preferably
10 torr or lower. The PTT thus obtained can show an
increase in the polymerization degree in terms of an
intrinsic viscosity of 0.1 dl/g or more compared with
that of the PTT at the end of melt polymerization. The
35   final intrinsic viscosity can be made to attain 1.5 dl/g
regardless of the intrinsic viscosity of the raw material
PTT. Moreover, the solid phase polymerization can reduce

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an amount of the cyclic dimer to less than 1.5% by weight.

Best Mode for Carrying Out the Invention

5   The present invention will be explained below by making reference to examples. However, the present invention is in no way restricted thereto. In addition, principal measured values in the examples were determined by the following procedures.

10   (1) Intrinsic Viscosity

Using an Ostwald viscometer and o-chlorophenol at 35°C, the ratio of a specific viscosity η_{sp} to a concentration C (g/100 ml) η_{sp}/C is measured, and the intrinsic viscosity [η] is obtained from the following

15   formula by extrapolating the concentration to zero:

$$[\eta] = \lim (\eta_{sp}/C)$$
$$C \rightarrow 0$$

(2) Content of Terminal Carboxyl Groups (-COOH)

Benzyl alcohol in an amount of 25 ml is added to 1 g

20 of a PTT, and the mixture is heated at 200°C for 15 minutes in a nitrogen atmosphere. Three drops of a phenolphthalein indicator and 25 ml of chloroform are added to the mixture, and the content of terminal carboxyl groups is determined by titrating with a 0.02 N

25 solution of potassium hydroxide in benzyl alcohol.

(3) Contents of Terminal Hydroxyl Groups ([-OH]) and Terminal Allyl Groups ([$-CH_2CH=CH_2$]) and peak areas of P1 and P2

A PTT is dissolved in a solvent mixture of

30 $CDCl_3/(CF_3)_2CDOD$ (volume ratio of 1:1), and measurements are made using ^{1}H-NMR (trade name of FT-NMR DPX-400, manufactured by Bruker). Tetramethylsilane is used as a reference.

(4) Amount of Bis(3-hydroxypropyl) Ether

35   A PTT in an amount of 2g is added to 25 ml of a 2N

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solution of potassium hydroxide in methanol, and the
mixture is refluxed for 4 hours so that solvolysis is
effected.   The amount is quantitatively determined by gas
chromatography using the methanol solution.   The amount
5   is measured with a column (trade name of BOND DB-WAX,
0.25 mm x 30 m (0.25 μm)) by heating a sample to
temperature from 150 to 230°C at a rate of 20°C/min while
helium is being allowed to flow at a rate of 100 ml/min.
A flame ionization detector is used as a detector.

10   (5) Oxidation Resistance Stability

A sample of the PTT thus obtained is held at 220°C
for 24 hours in the air.   The b* value of the sample
subsequent to the treatment is used as the index of
oxidation resistance stability.

15   (6) Melt Stability

The melt stability is evaluated by an accelerated
evaluation method as explained below.   Spinning a PTT is
conducted under the following conditions, and the melt
stability is evaluated.

20   Extrusion temperature: 265°C

Spinning nozzle: 36 holes having a diameter of 0.35
mmφ and a length of 0.7 mm being arranged in a single row

Discharge amount: 23 g/min

Winding rate: 4,000 m/min

25   Lowering rate of viscosity: the lowering rate being
obtained by cleaning the yarn thus obtained, measuring
the intrinsic viscosity, and calculating the rate from
the following formula:

melt stability (%) = (intrinsic viscosity of the
30   yarn)/(intrinsic viscosity of the raw material PTT
composition) x 100

Comparative Example 1

In a 3-liter autoclave equipped with a plate-like
blade shown in Fig. 1, 1,300 g (6.7 moles) of dimethyl
35   terephthalate (hereinafter abbreviated to DMT), 1,121 g
(14.7 moles) of PDO and 0.78 g of titanium tetrabutoxide

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were charged, and the ester interchange reaction was
conducted at 220°C while methanol was being distilled
off. The ester interchange reaction ratio was 95%.
After completion of the ester interchange reaction, 0.52

5   g of titanium tetrabutoxide and 0.65 g of trimethyl
phosphate were added to the reaction mixture, and the
contents were stirred for 30 minutes. The
polycondensation reaction was conducted at 260°C by
stirring the contents at 260°C, at a vacuum degree of

10   from 0.1 to 0.5 torr, with the blade rotated at 100 rpm,
while PDO was being distilled off. When the agitated
state of the polycondensation vessel was observed with a
video camera, the reactant formed a solution surface
without forming a film, and was rotated integrally (see

15   reference numeral 101 in Fig. 1). The integral rotation
took place because the agitating blade cannot rake the
reactant up due to its plate-like form.

The agitation torque increased with time during the
polycondensation reaction, and the polymerization degree

20   also increased. However, the agitation torque showed a
peaking phenomenon about 4 hours after starting the
polycondensation reaction. The agitation torque then
changed to decrease slightly. A PTT sample taken at the
stage where the agitation torque showed a peaking

25   phenomenon had an intrinsic viscosity of 0.8 dl/g, an L*
value of 87 and a b* value of 6.2. The formula (1) was
not satisfied in the PTT polymerization. For example,
the value of the left term in the formula (1) was 32%
when the polycondensation reaction was completed.

30   Moreover, the S/V ratio at the polymerization final stage
was 0.05 cm²/g.

Polymerization reaction was conducted separately
using a 1,000-liter polymerizer with the charging ratio
increased by a factor of 333. A similar phenomenon was

35   also observed, and a PTT sampled at the stage of peaking
phenomenon showed an intrinsic viscosity of 0.71 dl/g.
The formula (1) was not satisfied in the polycondensation

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reaction of the PTT. For example, the left term of the
formula (1) was 30% when the polycondensation reaction
was completed, and the L* and b* values were 87 and 7.8,
respectively. The S/V ratio in the polymerization final
5   stage was 0.01 cm²/g.

Furthermore, polymerization of the PBT was conducted
separately, under the same condition as that described
above except that 1,4-butanediol was used in place of PDO
in the same amount in terms of number of moles. The
10   condition was the same because the difference in melting
point between the PTT and the PBT was small. The
polymerization showed neither peaking of the agitation
torque nor lowering of the polymerization rate even when
polymerization was conducted for 4 hours. The polymer
15   then showed an intrinsic viscosity of 1.0 dl/g. No
peaking phenomenon was observed even when the scale of
the experiment was enlarged to 1,000 liters.

Polymerization of PET was conducted using the same
number of moles of ethylene glycol in place of PDO.
20   Because the melting point of the PET was higher by about
from 30 to 40°C than that of the PTT, the
polycondensation reaction temperature was set at 290°C.
Polymerization was conducted under the same conditions
except the reaction temperature. The polymerization of
25   the PET showed neither peaking of the agitation torque
nor lowering of the polymerization rate even when
polymerization was conducted for four hours. The
reactant showed an intrinsic viscosity of 1.0 dl/g when
the polymerization was conducted for 4 hours. No peaking
30   phenomenon was observed even when the scale of the
experiment was enlarged to 1,000 liters.

It can be understood from the explanation above that
the polymerization degree of the PTT is likely not to
increase, and that the tendency becomes important as the
35   polymerization scale is increased.

Table 1 summarizes the polymerization conditions and
the properties of the PTT thus obtained.

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Example 1

The procedure of Comparative Example 1 was repeated
by using the same reaction vessel (3 liters) as in
Comparative Example 1 and charging the same amounts of
5   reaction materials except that the reaction vessel was
equipped with a helical type-agitating blade shown in
Fig. 2. The measured values of the left term of the
formula (1) were 85, 75, 64 and 51% according as 1, 2, 3
and 4 hours elapsed after starting the polycondensation
10   reaction. The results showed that the formula (1) was
satisfied during the polycondensation reaction. In
addition, when the intrinsic viscosity was 0.5 dl/g or
more, the S/V ratio was from 0.17 to 0.24 cm^2/g. When
the polycondensation reaction was observed in the same
15   manner as in Comparative Example 1, a portion of the
reactant raised by the helical agitating blade dripped as
shown by a reference numeral 105 in Fig. 2 to form a
film. The film thickness was then confirmed to be 1 mm
or less by observation from a window in the upper part of
20   the vessel. The reactant in the vessel formed a large
recess in the central portion of the vessel, and the
surface area greatly increased. The reactant showed, 4
hours after the polycondensation reaction, an intrinsic
viscosity of 1.0 dl/g, an L* value of 90, a b* value of
25   2.1, an amount of BPE of 0.17% by weight and an amount of
the cyclic dimer of 2.63% by weight.

The polymerization reaction was separately conducted
by increasing the charging ratio by a factor of 1,333
using a polymerization vessel having a capacity of 4,000
30   liters obtained by similarly enlarging the former
reaction vessel. When the polycondensation reaction was
conducted for 4 hours, the PTT showed an intrinsic
viscosity of 0.95 dl/g, an L* value of 88 and a b* value
of 3,4. The polycondensation reaction of the PTT
35   satisfied the formula (1), and the left term of the
formula (1) at the stage of the completion of the
polycondensation reaction was 47%. Moreover, when the

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intrinsic viscosity of the reactant was 0.5 dl/g or more, the reactant showed an S/V ratio of 0.07 cm^2/g; the reactant contained 0.15% by weight of BPE, and 2.54% by weight of the cyclic dimer.

5   Table 1 summarizes the polymerization reaction conditions and the properties of the PTT.

Example 2

Bis(3-hydroxypropyl) terephthalate was allowed to continuously flow down at 251°C in a filmy state (see a

10   reference numeral 105 in Fig. 3) along a lattice (106) fixed to the central portion of a cylindrical reaction vessel (107) in Fig. 3, and fall into a reservoir provided under the reaction vessel. The atmospheric pressure within the cylindrical reaction vessel was

15   reduced to 0.5 torr, and the residence time during which the reaction solution falls into the reservoir was made 3 hours. When a portion of the reaction solution fell along the lattice, the state of a solution film was photographed with a video camera. The film thickness was

20   measured, and was 1mm or less. The polycondensation reaction was conducted while the formula (1) was being satisfied. For example, a sample was collected from the center of the lattice and another sample was collected from the reservoir, and the left term values of the

25   formula (1) were determined. The left term value of the former sample and that of the latter sample were 74 and 58%, respectively. The PTT in the reservoir showed an intrinsic viscosity of 1.2 dl/g, an L* value of 90 and a b* value of 2.3. The PTT thus obtained contained 0.18%

30   by weight of BPE and 2.42% by weight of a cyclic dimer.

Table 1 summarizes the polymerization reaction conditions and the properties of the PTT.

Example 3

In a 3-liter autoclave equipped with a helical type

35   agitating blade shown in Fig. 2, 1,112 g (6.7 moles) of terephthalic acid (hereinafter abbreviated to TPA), 1,121 g (14.7 moles) of PDO and 0.78 g of titanium

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tetrabutoxide were charged, and the ester interchange
reaction was conducted at 250°C while water was being
distilled off. The ester interchange reaction ratio was
97% or more in the reaction. After completion of the
5   ester interchange reaction, 0.52 g of titanium
tetrabutoxide was added, and the contents were stirred
for 30 minutes. The polycondensation reaction was
conducted at 260°C at a vacuum degree of from 0.1 to 0.5
torr while PDO was being distilled off and the formula
10   (1) was being satisfied.

     For example, the measured values of the left term of
the formula (1) were 83, 74, 61 and 52% according as 1,
2, 3 and 4 hours elapsed after starting the
polycondensation reaction. The values satisfied the
15   formula (1). When the state of agitation was observed in
the same manner as in Example 1, a portion of the
reactant raised by the helical agitating blade dripped to
form a film. The film thickness was 1 mm or less.
Moreover, a large recess was formed in the central
20   portion of the vessel, and the surface area greatly
increased. The reactant showed, 4 hours after starting
the polycondensation reaction, an intrinsic viscosity of
0.98 dl/g, an L^* value of 91 and a b^* value of 3.8, and
contained 0.74% by weight of BPE and 2.32% by weight of
25   the cyclic dimer.

     The polymerization reaction was separately conducted
by increasing the charging ratio by a factor of 1,333
using a polymerization vessel having a capacity of 4,000
1 prepared by similarly enlarging the former vessel.
30   When the polycondensation reaction was conducted for 4
hours, the PTT showed an intrinsic viscosity of 0.94
dl/g, an L^* value of 90 and a b^* value of 4.7. In
addition, the polycondensation reaction of the PTT was
conducted while the formula (1) was being satisfied. For
35   example, the left term of the formula (1) at the stage of
completion of the polycondensation reaction was 46%. The
PTT thus obtained contained 0.86% by weight of BPE and

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2.26% by weight of the cyclic dimer.

Table 1 summarizes the polymerization reaction conditions and the properties of the PTT.

Example 4

5   A PTT was produced at a rate of 20 ton/day by continuous polymerization from starting materials of TPA and PDO containing 300 ppm or less of carbonyl group-containing compounds, using a continuous polymerization apparatus shown in Fig. 4. Three vertical agitation

10   reaction apparatuses each having a spiral agitating blade were used for an esterification reaction vessel, a first and a second polycondensation reaction vessel, respectively. A horizontal agitation reaction apparatus having biaxial disc-like agitating blades was used for a

15   third polycondensation reaction vessel.

Polymerization was conducted as explained below. A mixture in a slurry state prepared by adding to a slurry of TPA and PDO in a molecular ratio (TPA:PDO) of 1:1.5, 0.1% by weight of titanium tetrabutoxide based on TPA was

20   continuously fed to the esterification reaction vessel, and polymerization was conducted at 230°C under normal pressure for a residence time of 200 minutes while water was being discharged to give bis(3-hydroxypropyl) terephthalate and its oligomer having an intrinsic

25   viscosity of 0.10 dl/g. Thereafter, 0.5% by weight of titanium oxide as a delustering agent and 20 ppm of trimethyl phosphate based on the PTT were added to the reactant. The reaction mixture was continuously introduced into the first polycondensation reaction

30   vessel, and subjected to a polycondensation reaction at 250°C under reduced pressure of 300 torr for a residence time of 60 minutes. The reactant (having an intrinsic viscosity of 0.15 dl/g) thus obtained was continuously introduced into the second polycondensation reaction

35   vessel, and subjected to a polycondensation reaction at 250°C under reduced pressure of 20 torr for a residence time of 60 minutes. The reactant (having an intrinsic

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viscosity of 0.30 dl/g) thus obtained was further
continuously introduced into the third polycondensation
reaction vessel, and subjected to a polycondensation
reaction at 260°C under reduced pressure of 1.5 torr for
5   a residence time of 60 minutes. The left term value of
the formula (1) was 68% at the final stage of the
polycondensation reaction. The reactant in the third
polycondensation reaction vessel showed an intrinsic
viscosity of 0.5 dl/g or more and an S/V ratio of 1.5
10   cm^2/g when the reactant passed 1/3 of the polymerization
vessel. The PTT finally obtained showed an intrinsic
viscosity of 0.95 dl/g. an L^* value of 88 and a b^* value
of 2, and contained 1.1% by weight of BPE. The present
polymerization process can be continuously operated for
15   one year or more.

Table 1 summarizes the polymerization reaction
conditions and the properties of the PTT.

Example 5

A PTT was produced at a rate of 20 ton/day by
20   continuous polymerization from starting materials of
dimethyl terephthalate and PDO containing 300 ppm or less
of carbonyl group-containing compounds, using a
continuous polymerization apparatus shown in Fig. 4.
Three vertical agitation reaction apparatuses each having
25   a spiral agitating blade were used for an esterification
reaction vessel, a first and a second polycondensation
reaction vessel, respectively. A horizontal agitating
reaction apparatus having biaxial disc-like agitating
blades was used for a third polycondensation reaction
30   vessel.

Polymerization was conducted as explained below.
Molten DMT at 180°C, PDO at 190°C and 0.1% by weigh of
titanium tetrabutoxide based on DMT were continuously fed
to the esterification reaction vessel so that the
35   molecular ratio of DMT:PDO became 1:2.5, and
polymerization was conducted at 230°C under normal
pressure for a residence time of 100 minutes while

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methanol was being discharged to continuously give bis(3-hydroxypropyl) terephthalate and its oligomer having an intrinsic viscosity of 0.08 dl/g.

  Thereafter, 0.5% by weight of titanium oxide, as a delustering agent, and 20 ppm of trimethyl phosphate based on the PTT were added to the reactant. The reaction mixture was continuously introduced into the first polycondensation reaction vessel, and subjected to a polycondensation reaction at 250°C under a reduced pressure of 300 torr for a residence time of 60 minutes. The reactant (having an intrinsic viscosity of 0.1 dl/g) thus obtained was continuously introduced into the second polycondensation reaction vessel, and subjected to a polycondensation reaction at 250°C under reduced pressure of 20 torr for a residence time of 60 minutes. The reactant (having an intrinsic viscosity of 0.30 dl/g) thus obtained was further continuously introduced into the third polycondensation reaction vessel, and subjected to a polycondensation reaction at 260°C under reduced pressure of 1.5 torr for a residence time of 60 minutes. The left term value of the formula (1) was 68% at the final stage of the polycondensation reaction. The reactant in the third polycondensation reaction vessel showed an intrinsic viscosity of 0.5 dl/g or more and an S/V ratio of 1.5 cm²/g when the reactant passed 1/3 or more of the polymerization vessel. The PTT finally obtained showed an intrinsic viscosity of 0.95 dl/g, an L* value of 90 and a b* value of 2.5, and contained 0.25% by weight of BPE and 2.56% by weight of the cyclic dimer. The present polymerization process can be continuously operated for one year or more.

  Table 1 summarizes the polymerization reaction conditions and the properties of the PTT.

  Example 6

  The pellets of the PTT obtained in a 4,000-liter polymerization vessel in Example 1 were subjected to solid phase polymerization at 205°C in a nitrogen gas

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flow at a rate of 10 l/min for 30 hours. The PTT thus
obtained showed an intrinsic viscosity of 1.35 dl/g, a
left term in the formula (1) of 42%, an L* value of 92
and a b* value of 1.2, and contained 0.16% by weight of
5   BPE and 1.00% by weight of the cyclic dimer. The PTT
thus obtained was excellent in both the oxidation
resistance stability and melt stability (melt spinning
being conducted at 290°C).

      Table 1 summarizes the polymerization reaction
10   conditions and the properties of the PTT.

      Example 7

      The pellets of the PTT obtained in a 4,000-liter
polymerization vessel in Example 3 were subjected to
solid phase polymerization at 205°C in a nitrogen gas
15   flow for 40 hours. The PTT thus obtained showed an
intrinsic viscosity of 1.39 dl/g, a left term in the
formula (1) of 48%, an L* value of 92 and a b* value of
0.7, and contained 0.77% by weight of BPE and 0.97% by
weight of the cyclic dimer. The PTT thus obtained was
20   excellent in both the oxidation resistance stability and
melt stability (melt spinning being conducted at 290°C).

      Table 1 summarizes the polymerization reaction
conditions and the properties of the PTT.

      Example 8

25   The same reaction vessel (3 liters) as in
Comparative Example 1 was used except that the reaction
vessel was equipped with a helical agitating blade shown
in Fig. 2, and the same charging amount as in Comparative
Example 1 was used provided that the rotation rate of the
30   blade was lowered to 5 rpm during the polycondensation
reaction; the same investigation as therein was carried
out. The measured values of the left term of the formula
(1) were 78, 70, 52 and 41% according as 1, 2, 3 and 4
hours elapsed after starting the polycondensation
35   reaction. The results showed that the formula (1) was
satisfied during the polycondensation reaction. The S/V
ratio was 0.05 cm^2/g when the intrinsic viscosity was 0.5

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dl/g or more.

When 4 hours elapsed after starting the polycondensation reaction, the PTT showed an intrinsic viscosity of 0.83 dl/g, an L* value of 87 and a b* value of 4.6, and contained 0.17% by weight of BPE and 2.65% by weight of the cyclic dimer.

Table 1 summarizes the polymerization reaction conditions and the properties of the PTT.

Comparative Example 2

In the experiment on a 1,000-liter scale in Example 1, the procedure of Example 1 was repeated except that the polymerization temperature was set at 282°C, and that the polycondensation reaction was conducted for 2 hours. The left term of the formula (1) was 30% when the polymerization was finished.

The PTT thus obtained showed an intrinsic viscosity of 0.80 dl/g, an L* value of 87 and a b* value of 8.7, and contained 0.17% by weight of BPE and 2.67% by weight of the cyclic dimer. The PTT thus obtained showed insufficient oxidation resistance stability and melt stability. Moreover, the PTT was subjected to solid phase polymerization at 205°C in a nitrogen gas flow for 40 hours. The resultant PTT showed an intrinsic viscosity of not greater than 1.21 dl/g. Furthermore, the left term of the formula (1) was 27.

Table 1 summarizes the polymerization reaction conditions and the properties of the PTT.

Example 9

The PTT obtained in Example 1 was injection molded to form gears and connectors. The molded articles thus obtained were excellent in whiteness, and showed no substantial change in color when heated in the air at 130°C for 24 hours. In contrast to the above articles, molded articles prepared from the PTT in Comparative Example 1 in the same manner as explained above were colored yellow, and showed a significant increase in yellowness when treated at 130°C in the air for 24 hours.

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Example 10

A film prepared by injecting the PTT obtained in Example 1 at 265°C through a die, 0.2 mm (width) x 50 mm (length), was drawn at 135°C in the longitudinal
5 direction in a ratio of 1.5 and in the transverse direction in a ratio of 1.2 to give a tough film. The film thus obtained was not colored, and showed no substantial change in color when treated in the air at 130°C for 24 hours. In contrast to the above film, a
10 film prepared from the PTT obtained in Comparative Example 1, in the same manner as explained above was colored yellowish, and became significantly yellowish when treated at 130°C in the air for 24 hours.

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Table 1

Ex.	Polymerization conditions				Properties of polymer							
	Amt. of DMT or TPA (kg)	Polymerization temp. (°C)	X value* (%)	S/V (cm²/g)	[η] (dL/g)	X value (%)	L*	b*	Amt. of BPE (wt.%)	Melt stability (%)	Oxidation resistance	Amt. of cyclic dimer (wt.%)
1	1.3	260	51	0.17-0.24	1.0	51	90	2.1	0.17	94	17	2.63
	1733	260	47	0.07	0.95	47	88	3.4	0.15	93	18	2.54
2	-	251	58	0.25	1.2	58	90	2.3	0.18	94	18	2.42
3	1.1	260	52	0.18-0.25	0.98	52	91	3.8	0.74	93	19	2.32
	1482	260	46	0.13-0.21	0.94	46	90	4.7	0.86	90	20	2.26
4	-	260	68	1.5	0.95	68	88	2	1.1	94	19	-
5	-	260	74	1.5	0.95	74	90	2.5	0.25	96	16	2.56
6	-	-	-	-	1.35	42	92	1.2	0.16	88	17	1.00
7	-	-	-	-	1.39	48	92	0.7	0.77	87	16	0.97
8	1.3	260	41	0.05	0.83	41	87	4.6	0.17	87	21	2.65
C.E. 1	1.3	260	32	0.05	0.8	32	87	6.2	0.23	82	24	2.67
	433	260	30	0.01	0.71	30	87	7.8	0.30	83	23	2.78
2	1.3	282	30	0.12-0.19	0.80	32	87	8.7	0.17	81	26	2.67

Note: *: X value = [-OH]/([-OH] + [-COOH] + [-CH₂CH=CH₂]) × 100
          (measured when polymerization is completed)

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Industrial Applicability

The present invention can provide a PTT having a molecular weight in a range from low to high and excellent in shade, oxidation resistance stability and
5   melt stability even when the PTT is prepared by polymerization on an industrial scale. Moreover, because the solid phase polymerization rate of PTT is high, a PTT having a still higher molecular weight can be provided without suffering much thermal decomposition. The PTT
10   thus obtained can be used for any of the applications such as fiber formation, resin molding and film formation.